BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :
A23L 1/304, A23D 7/00, 7/015, 7/02, A23L 2/52, 2/66, A23C 9/13

A1

(11) International Publication Number: **WO 00/45650**

(43) International Publication Date: 10 August 2000 (10.08.00)

(21) International Application Number: PCT/GB00/00355

(22) International Filing Date: 7 February 2000 (07.02.00)

(30) Priority Data:
9902670.0 6 February 1999 (06.02.99) GB

(71) Applicant *(for all designated States except US)*: NUTRA-HEALTH LTD. (UK) [GB/GB]; 3 Sun Gardens, Burghfield Common, Reading, Berkshire RG7 3JB (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: ERMOLAEVA, Svetlana A. [RU/RU]; Tayninskaya, 98–113, Moscow, 129345 (RU). VULFSON, Evgeny Naum [RU/GB]; The Old School House, Mill Road, Marlingford, Norwich NR9 5HL (GB).

(74) Agent: MILES, John, S.; Eric Potter Clarkson, Park View House, 58 The Ropewalk, Nottingham NG1 5DD (GB).

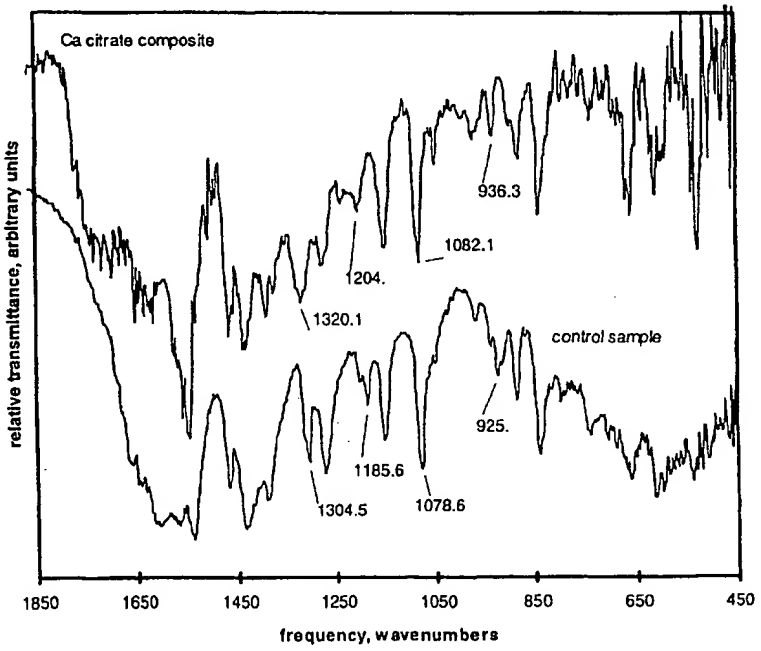
(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: CALCIUM SUPPLEMENTED FOOD PRODUCTS AND NOVEL CALCIUM–CONTAINING INGREDIENT

(57) Abstract

This invention relates to food products and drinks in general and particularly to an emulsified fat spread which are supplemented with calcium and a process for the preparation thereof. This invention also relates to a novel calcium–containing ingredient and a method for its preparation and its use in the above said products and processes. Combining a source of calcium ions and a source of anions in an aqueous solution of milk derived solids, proteins or other suitably functionalised food additives, and using the resulting suspension as an aqueous phase for the preparation of an emulsified fat spread.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

CALCIUM SUPPLEMENTED FOOD PRODUCTS AND NOVEL CALCIUM-CONTAINING INGREDIENT

FIELD OF THE INVENTION

This invention relates to food products and drinks (or beverages) in general and particularly to an emulsified spreadable food product which are supplemented with calcium and a process for the preparation thereof. This invention also relates to a novel calcium-containing ingredient and a method for its preparation and its use in the above said product and process.

BACKGROUND OF THE INVENTION

Calcium is an essential element in the human diet. It is necessary for the regulation of numerous metabolic functions in the body such as muscle contraction, blood clotting and neural transmission and also for normal growth and development of bones and teeth. In recent years calcium has received much attention due to its role in the prevention of bone mass reduction (osteoporosis). In the USA alone, osteoporosis affects about 25 million people and it is the major cause of bone fracture in elderly and post menopausal women. It is generally accepted that the occurrence of osteoporosis is dependent on the attainment of optimal bone mass in the early years of life and on the rate of its loss in later years. It is also generally accepted that an adequate dietary intake of calcium is an important preventive factor and consequently the fortification or supplementation of food products with calcium has become a common practice in recent years. The

recommended daily intake of calcium varies from country to country. For example, the recommended daily uptake of calcium for adolescents/young adults in Britain is 1000 mg for men and 800 mg for women and it is even higher (1200-1500 mg) for the same categories of people in the USA.

Many calcium sources are currently used for the fortification or supplementation of food products. Some eg calcium carbonate, calcium phosphate and calcium citrate and other organic acid salts of calcium are poorly water soluble at neutral and slightly acidic pH which are most common in food formulations. These salts, if precipitated in the aqueous phase of a food or drink or when used in food or drink in insoluble form, create an undesirable sensation of powderiness in the mouth, so-called "chalky" mouth feel. Other calcium sources eg calcium chloride, calcium acetate and a few organic acid salts of calcium are soluble in water in substantial quantities. However, at high concentrations they have poor organoleptic properties and also interact with other food components such as, for example, proteins leading to their precipitation and coagulation.

Among various calcium-fortified food formulations available to consumers, drinks remain the most numerous. This is due to the relative ease of formulating a drink composition of acceptable organoleptic quality which contains about 1% (w/w) of a water soluble calcium salt to provide a substantial part of the recommended daily uptake of calcium in several hundred cm^3 of the liquid product. However, in many countries, notably in Europe, calcium fortified drinks are not consumed by a large proportion of the population on a regular basis. Thus, there is a need in the trade to develop

and introduce new products to enable more people to benefit from calcium-supplemented foods. It is also desirable for these food products to be an integral part of people's diet so that they can draw the maximum benefit from calcium fortification with minimum expense. Fat spreads are particularly suitable vehicles for the incorporation of calcium as they are consumed by a large number of people on a daily basis.

Fat spreads and margarine can be prepared with different fat contents as legally specified, typically between 10% and 80% fat by weight, and the products can be labelled accordingly as, for example, low fat or very low fat spreads. The latter are especially appealing to many health conscious consumers. Generally, depending on the fat content and other ingredients used, a fat spread is a water-in-oil or oil-in-water emulsion (or a combination of the two) which has a butter like consistency and taste and which is spreadable. The daily intake of butter and fat spreads varies from country to country but a typical adult consumes about 25 gram of butter or butter like product a day. Thus, to provide a substantial part of the recommended daily intake of calcium, a fat spread should contain several gram of calcium source per 100 gram of product, depending on the calcium content of the source. Given that the water content of a typical spread is only about 30% and of a typical low fat spread is about 60%, a highly concentrated solution or suspension of the calcium source in water or in oil must be used to provide the consumer with the health benefits sought.

Recently Cante *et al* (EP 0 549 290) disclosed a calcium citrate-vegetable oil composition which is spreadable. According to the invention of

Cante *et al* a new crystalline calcium citrate in the form of distinct platelets of about 1 by 1.5 micron, can be obtained by combining a source of calcium ions and citric acid in a mole ratio from 2.5:2 to 2.95:2 under carefully controlled conditions of pH and temperature. It is claimed (EP 0 549 290) that the thus obtained crystalline calcium citrate, when admixed into vegetable oils, results in a significant increase in the viscosity of the oil and this admixture gives a semi-solid fat product which is spreadable. However, the invention of Cante *et al* can only be practised with the disclosed calcium citrate platelets of defined size, shape and composition. Also, according to the invention of Cante *et al* the calcium citrate platelets must be incorporated into the oil to obtain the desirable increase in viscosity ie to produce a spreadable product. Also, according to the invention of Cante *et al* the product does not contain a mixture of vegetable oil and hardened fat which is necessary to provide the butter-like sensation in the mouth on melting. Also, according to the invention of Cante *et al* the product is not an emulsified spread and it is manufactured by a process which is different from those employed for the production of conventional fat spreads. The present invention provides a novel fat spread which is an emulsified product and has a butter like taste and can be prepared with a variety of calcium sources and where the above said calcium sources are not platelets of defined composition, size and shape and where the calcium source is incorporated into the aqueous phase of the fat spread. The present invention also provides a novel calcium-containing ingredient and a method for the preparation thereof and its use in food products and drinks.

SUMMARY OF THE INVENTION

This invention relates to the discovery that by combining a source of calcium ions and a source of anions in an aqueous solution of milk derived solids, proteins or other suitably functionalised food additives, and using the resulting suspension as an aqueous phase for the preparation of an emulsified fat spread, a spread with good organoleptic properties and no undesirable chalky sensation in the mouth is produced. According to this invention the calcium source is incorporated into the aqueous phase of the fat spread in a largely insoluble form prior to emulsification. This invention also provides a process for the preparation of calcium-supplemented or fortified fat spreads with acceptable organoleptic properties. This invention also provides a novel calcium-containing ingredient and a method for the preparation thereof and its use in food products and drinks.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to the discovery that by combining a source of calcium ions and a source of anions ie counterions in an aqueous solution of milk derived solids (or other suitable food additives as defined below), and using the resulting suspension as an aqueous phase for the preparation of an emulsified fat spread, a spread with good organoleptic properties and no undesirable chalky sensation in the mouth is produced. This is a surprising finding because it is well known in the art that the organoleptic properties of emulsified fat spreads are very sensitive to the composition of the aqueous phase. Thus, when a fat spread is prepared with commercially available

calcium salts such as, for example, calcium citrate, calcium phosphate and calcium carbonate, at a loading of about 4 gram per 100 gram of spread, the resulting product has poor organoleptic properties. The addition of milk solids, for example sodium caseinate, whey or whey proteins does not significantly improve the organoleptic properties of the product which remains chalky. It was found that the sensation of powderiness in the mouth can be somewhat reduced but not eliminated completely by incubating the above mentioned calcium salts in an aqueous solution of milk derived solids, preferably from about 2% to about 10% by weight. However, when the individual constituents of the same calcium salts are combined and precipitated in the aqueous solution of milk derived solids under the same conditions, a good fat spread is obtained and no sensation of powderiness is detected by organoleptic assessment of the product. This is a very surprising finding because the chemical composition of the two above said preparations is identical as they contain the same amounts of the calcium ions source, the source of anions and milk derived solids.

It was found, for example, that a fat spread with good organoleptic properties can be obtained by adding $Ca(OH)_2$ to an aqueous solution of whey powder, preferably of high protein content, or milk-derived proteins such as caseins or their salts, in citric acid, preferably at a temperature between about 50°C and about 95°C with stirring. The contact time can be as short as 15-45 minutes or substantially longer, if desired. It was further found that the initial source of calcium ions and counterions (anions) is not crucial for practising the present invention. Thus, suitable calcium containing

ingredients and fat spreads with good organoleptic properties are obtained when using $CaCl_2$, $CaCO_3$ or CaO as a source of calcium ions and organic acids such as, for example, citric acid or malic acid or a mixture thereof in any molar ratio or inorganic acid such as phosphoric acid as a source of anions (counterions). Salts of organic and inorganic acids can also be successfully used. For example, $CaCl_2$ can be combined with Na_2CO_3 or NaH_2PO_4, or sodium citrate or sodium malate. Also, various milk derived solids such as, for example, milk powder, casein, sodium caseinate, whey, whey protein, butter milk and the like can all be successfully employed. The above said calcium preparations are largely water insoluble. In the context of this invention, the term "largely water insoluble" is understood to mean a calcium preparation or salt which, at the concentration used, remains substantially insoluble in an aqueous solution of pH from about 3 to about 9 at temperatures used for the storage and consumption of the product, typically from about 4°C to about 30°C. Typically, in the food product, at least 90% of the calcium composite remains insoluble.

It was further found that the fat spreads according to the present invention can be further fortified or supplemented with water soluble calcium salts, both inorganic, such as, for example, $CaCl_2$ and organic such as, for example, metastable calcium citrate malate (US 4 722 375), without affecting the organoleptic properties of the product. In the context of this invention, the term "water soluble salt" is understood to mean a salt which, at the concentration used, is substantially soluble (and, preferably substantially completely soluble) in an aqueous solution of pH from about 3 to about 9

temperatures used for the storage and consumption of the product, typically from about 4°C to about 30°C. The combination of water soluble and largely water insoluble salts and sources can be used, if desired, to further increase the overall calcium content of the spread. Both largely water insoluble and water soluble calcium salts and sources can be calcium salts of organic and inorganic acids and these salts can be combined in any combination. For example, water soluble calcium chloride or metastable calcium citrate malate or a mixture thereof can be employed either with inorganic calcium phosphate or organic calcium citrate containing composites according to this invention, or a mixture thereof.

An extensive study and research has been conducted to elucidate the effect of milk solids on the calcium source and explain the difference in the taste perception. Without wishing to be bound by or advance any theory, it is believed that multifunctional components and particularly proteins which are present in milk derived solids interact with nucleation sites or small crystals or particles of calcium salts formed in aqueous solution and this interaction alters the normal course of crystallisation or precipitation. It is known for example, that in Nature proteins are incorporated into a largely crystalline matrix of calcium carbonate in, for example, shells of molluscs by a process which is not yet well understood and this incorporation results in the formation of composite mineral-organic materials of complex structure. It is likely therefore that multifunctional compounds which are present in milk derived solids eg proteins exert a significant influence on the morphology of the resulting calcium containing material by forming a protein/calcium source

composite with a distinctly different structure and sensory properties. It is further asserted that proteins from other sources eg soya protein or other plant-derived proteins, and other protein containing food solids and protein derivatives such as, for example, their acid or enzymatic hydrolysates and other food additives which bare one or more of the same functional groups ie carboxyl, hydroxyl, amino, amido, thiol or phenol groups, when added to an aqueous solution prior to combining a calcium ion source with a source of anions, should exert a similar influence on the morphology of calcium composites and influence the organoleptic properties of the above said calcium composites, when incorporated in emulsified fat spreads and other food and drink formulations. The additive is any suitable additive which is acceptable in food and have the functionality as disclosed herein. Preferably, the additive has at least two, more preferably at least three and still more preferably at least four of the functional groups described above. Typically, the additive is one which has been or will be approved for food use. The additive may be a proteolytic fragment of a protein or a peptide derived from a protein. Proteolytic fragments or peptides derived from a protein which are long enough to retain some element of secondary structure are preferred.

For the avoidance of doubt, the additive is not an insolubilizing anion as herein defined. In other words, the term additive does not include simple inorganic or organic anions such as phosphate, carbonate, sulphate, pyrophosphate, citrate, malate, lactate, citrate malate, propionate, gluconate, succinate, or ascorbate or mixtures thereof.

Examination of the calcium citrate-whey protein composite by, for

example, SEM microscopy revealed a material of entirely different structure to that of a chemically identical sample of calcium citrate (control sample) precipitated in the absence of whey powder and subsequently treated with solution of whey powder under the same conditions. At lower magnification the composite material appears smooth with virtually no particulate matter observed and at higher magnification, ribbons or filaments of well structured, probably crystalline or partially crystalline matter are clearly seen. This is entirely different from the structure of whey protein-treated calcium citrate which is appears relatively coarse at lower magnification and which essentially consists of calcium citrate crystals of typical size and shape. The structural differences in the two above said materials of the same chemical composition can also be observed by other physico-chemical methods, for example, FT-IR. The FT-IR spectrum of the control sample shows the same characteristic bands occurring at essentially the same frequencies as a commercially obtained sample of calcium citrate (Sigma Chemical Co). In the spectrum of the calcium citrate-whey protein composite some of the bands were shifted in frequency or were absent or were replaced by new bands.

Thus a calcium composite according to this invention consists of a largely insoluble mixture of calcium, an insolubilizing anion and protein (or other suitable additive) where typically the co-precipitation of both components has altered the physical state of one or more components. Such physical changes may include the morphology, habit or crystal size or degree of crystallinity of the calcium and are apparent from the examination of the materials by methods such as FT-IR spectroscopy and SEM. Calcium

composites therefore differ from material of the same chemical composition which is obtained by, for example, coating crystals of the calcium salt with protein after precipitation of the calcium salt in that the thus coated crystals exhibit the same physical characteristics as the uncoated salt as apparent from FT-IR spectroscopy and other techniques. A sample of the calcium citrate-whey protein composite which had been spray dried also showed the same characteristic frequency shifts and pattern of bands in the FT-IR as the composite described above. Thus the composite was unaffected by the drying process.

By "insolubilizing anion" we mean an anion which, when present with a calcium ion, leads to a substantially aqueous-insoluble salt.

The invention also includes a calcium composite material which comprises a calcium salt and an additive where the additive is as defined above.

The calcium composite of the present invention can be produced in a separate process or, for example, as a part of the fat spread (or other food and drink) manufacturing process ie directly in an aqueous solution which is to be used as an aqueous phase of the fat spread. It is preferred to make the composite first and to add other additives such as, for example, water soluble flavours, thickeners or NaCl at a later stage. In the case when a calcium source is combined with salts of organic and inorganic acids, preferably sodium salts, it may not be necessary to add additional NaCl to the aqueous phase composition. The calcium composite of the present invention can also be produced separately and dried or partially dried by any conventional drying

method. In this case, the above said composite can be added to an aqueous phase of fat spreads or other food or drink as a solid or a paste either before or after the addition of other additives, depending on the preference of those making the spread or other food or drink. A homogenisation step may be desirable to reduce the particle size of the composite preparation. Any conventional homogenisation technique can be successfully employed.

The calcium composite of the present invention as obtained or in dry form or as a paste can be used for the manufacture of a wide range of food and drink products such as, for example, fermented and non-fermented dairy products, alcoholic and non-alcoholic drinks, soups, sauces, dips, salad dressings, mayonnaise, non-fat spreads, confectionery, bread, cakes, biscuits and breakfast cereals, to obtain foods and drinks which are supplemented with calcium. The use of calcium containing composites of the present invention in foods and drinks constitute yet another aspect of this invention. For example, a yoghurt or a yoghurt drink can be fortified or supplemented with the calcium composite of the present invention and the resulting products have a texture, flavour and appearance which is similar to or substantially indistinguishable from the corresponding product compositions prepared with no composite added. Although the present invention is illustrated by the preparation of fat spreads, yoghurt and yoghurt drinks, those skilled in the art will instantly recognise that it can be successfully practised with many other food and drink products and as a food supplement in, for example, the form of tablets and capsules. It will be appreciated that the calcium salt composite may be produced *in situ* during the preparation or manufacture of the food

product or beverage (or drink), or it can be added separately during the manufacturing or preparation process. The terms drink and beverage are used interchangeably in this specification.

The fat spreads according to this invention can be made with a different fat content, preferably with a fat content below 40%. Conventional vegetable oils such as, for example, sunflower oil, soybean oil, rape seed oil and the like can all be used as obtained or after hardening or any other chemical or physical treatment, as known and acceptable in the art. Animal fats, preferably butter fat, may also be used. Other ingredients can be optionally added to the oil phase. Examples of the above said ingredients include flavouring and colouring agents and vitamins, preferably those which are conventionally used in the manufacture of fat spreads.

When producing low and very low fat spreads according to this invention it is preferred to use stabilisers. The stabilisers which can be used to practice the present invention include gelatine, maltodextrins, starch and modified starch, cellulose and its derivatives and pectins and their derivatives and other polysaccharides of plant or seaweed origin. However, this is not an exhaustive list and those skilled in the art will instantly recognise that other stabilisers as well as various mixtures thereof can also be successfully employed.

Conventional emulsifiers, preferably mono/di-glycerides (E471), lecithin (E322) and polyglycerol esters (E476), can be used to produce the fat spreads according to this invention, preferably using the process of this invention. The above said emulsifiers can be used on their own or as a

mixture or any combination thereof or in conjunction with other suitable emulsifiers which are known in the art. The emulsifier can be added to the oil phase or to a part of the oil phase or to the aqueous phase, preferably after combining a source of calcium ions with a source of anions and milk derived solids.

The spreads according to this invention can be prepared to contain vitamins, such as vitamins A and D, which are conventionally incorporated into fat spreads or are required to be added by legislation. In addition the spreads and other food products and drinks according to this invention can be further supplemented with any other additives known to be beneficial to human health. For example, plant sterols or their esters can be included, if desired, to provide the additional benefit of lowering cholesterol or additional vitamins and minerals, carotenoids (eg lycopenes, α-tocopherol), antioxidants (eg ascorbic acid, flavonoids and isoflavones), lutein and other phytochemicals, which are known be beneficial to human health, can all be used. In the context of this invention the term "beneficial to human health" is understood to mean any physiologically active compound which is not a nutrient and can be shown to prevent or reduce the risk or ameliorate the conditions or symptoms of a disease when taken regularly as a part of the diet. The above said physiologically active compounds do not have to be co-precipitated or co-crystallised with the calcium-containing composites of the present invention and can be added separately to the food product or beverage (or drink) of the present invention at an appropriate manufacturing stage. For example, water soluble additives such as, for example, vitamins

and other minerals can be incorporated into the aqueous phase prior to emulsification, preferably after combining a source of calcium ions with a source of anions in a solution containing milk derived solids according to the present invention.

It will be appreciated that the calcium composite of the present invention is incorporated in the food and drink products at an appropriate stage of the manufacturing process. For example, in the production of yoghurt, the composite can be added to milk prior to fermentation with lactic acid bacteria or much later at the stage of breaking the coagulum, if a stirred yoghurt is desired.

The calcium composites of the invention may conveniently be used in food supplements. Typically, the food supplements are tablets containing the composite and suitable binding agents which allow the composite to bind and form a tablet. The tablet may also contain other ingredients such as colouring or flavouring or other ingredients known in the art. Conveniently, the tablet may also be coated, for example with a candy coating. The food supplements may also be capsules, in which case the calcium composite is present within the capsule either alone or in combination with some other agent such as a flavouring agent. The food supplement may also be a suspension of the calcium composite in a food-acceptable liquid. For example, the calcium composition may be in aqueous suspension. The food supplements may conveniently contain other desirable components such as vitamins, minerals, carotenoids and the like as herein disclosed.

The present invention is further illustrated by specific examples and

figures which are provided herein exclusively for the purpose of illustration and are not intended to be limiting. Any person sufficiently skilled in the art will recognise that numerous alterations to conditions and protocols presented herein can be introduced within the spirit and scope of the present invention.

FIGURE LEGENDS

Figure 1 is a Fourier transform infra red (FT-IR) spectrum of air dried composite and control materials.

Figure 2 shows SEM (scanning electronic microscope) photomicrographs of the air-dried composite and control materials. (a) and (c) are the composite and (b) and (d) are the control sample. (a) and (b) are at lower magnification and (c) and (d) are at higher magnification (see scale bars).

Figure 3 shows SEM photomicrographs of calcium phosphate (control; top); calcium phosphate/whey composite (middle); and calcium phosphate + whey protein (control; bottom). Further details are given in Example 5 (the left hand side are at lower magnification and the right hand side is at higher magnification; see scale bars).

Figure 4 shows SEM photomicrographs of calcium carbonate + whey (control; left) and calcium carbonate/whey composition (right) at different magnifications (see scale bars). See Example 6 for further details.

EXAMPLES

Example 1.

Preparation of the calcium citrate composite: Whey protein concentrate (Alacen, New Zealand Dairy Products; 56 g/L) was dissolved in an aqueous solution of citric acid monohydrate (210.16 g/L) and heated to 60°C. 77.88 gram of $Ca(OH)_2$ was added and the resulting mixture was stirred for a further 45 minutes. A control sample of whey protein-coated calcium citrate was prepared in exactly the same way except whey protein concentrate was added after combining the aqueous solution of citric acid and $Ca(OH)_2$ and the sample containing calcium citrate precipitate and whey powder was incubated for 45 minutes at 60°C. The SEM photomicrographs are shown in Figure 1 and FT-IR spectra of the air-dried composite and control materials are shown in Figure 2.

Example 2.

Whey protein (56 g/L) was dissolved in an aqueous solution of citric acid monohydrate (210.16 g/L) and heated up to 60°C. 77.88 gram of $Ca(OH)_2$ was added and the resulting mixture was stirred for a further 45 minutes. NaCl (4.5%) was added, the pH adjusted to 5.8, and 30 parts of this suspension was emulsified with 70 parts of an oil mixture consisting of sunflower oil (79%) and hydrogenated vegetable oil (21%). Emulsifiers E471 and E322 (0.5%), fat soluble butter flavours (0.035%) and colouring (0.04%) were included in the oil.

Example 3.

A fat spread was prepared as described in Example 2 but the suspension containing calcium citrate was first diluted 1:1 with water, gelatine (3%) and NaCl (2.5%) was added, and 62 parts of the resulting aqueous phase was emulsified with 38 parts of oil using E471 and E322 (1%) as emulsifiers.

Example 4.

A calcium citrate composite was prepared as described in Example 1 but a mixture of citric acid monohydrate (105.1 g/L) and malic acid (55.1 g/L) at 1:1 molar ratio was used. A fat spread was prepared as described in Example 3.

Example 5.

A calcium phosphate-whey protein composite was prepared as described in Example 1 but using 104 g/L of $NaH_2PO_4x2H_2O$ instead of citric acid monohydrate (210.16 g/L). A solution of NaH_2PO_4 (265.3 g) was dissolved in water (2000 mL) and to this solution whey protein (140 g; 56g/L final concentration) was added. The mixture was heated up to 60°C with stirring, $CaCl_2x6H_2O$ (558.9 g) was added slowly and the volume was made up to 2500 mL with water. The stirring was continued for a further 45 min, after which time the suspension was cooled down to room temperature with stirring. The resulting calcium phosphate/protein composite was washed with water to remove the excess of salt, gelatine (3%) and citric acid (1%) were

added, the pH was adjusted to 5.8 and a fat spread was prepared as described in Example 3. SEM microphotographs of the calcium phosphate/whey composition, calcium phosphate and calcium phosphate crystals with whey protein added after the crystallisation was completed (controls) are shown in Figure 3.

Example 6.

A calcium carbonate-whey protein composite was prepared as follows: a solution of $NaHCO_3$ (168 g) in water (800 mL) was prepared. This was heated gently to about 40°C to aid the dissolution of the salt. To this solution protein-rich whey powder (56 g; 56 g/L final concentration) was added and the mixture was heated up to 60°C with stirring. $CaCl_2x6H_2O$ (223 g) was then added slowly and a little water to give a final volume of 2500 ml. The stirring continued for further 45 min and the suspension was cooled down to room temperature with stirring. The resulting calcium carbonate/whey composite was washed with water to remove the excess of sodium chloride and the pH was adjusted to 5.8 by adding solid citric acid. After appropriate dilution and addition of gelatine, the composite was used for the preparation of fat spread as described in Example 3. SEM microphotographs of the calcium carbonate/whey composite and calcium carbonate crystals with whey added after the crystallisation was completed (calcium carbonate + whey control) are shown in Figure 4.

Example 7.

A calcium citrate composite was prepared as described in Example 1 but sodium caseinate (60 g/L) was used instead of whey powder and the solution of sodium caseinate in citric acid and $Ca(OH)_2$ were combined at 90°C rather than 60°C. A fat spread was prepared as described in Examples 2 and 3.

Example 8.

A fat spread was prepared as described in Example 3 but the amount of NaCl in the aqueous phase was reduced to 0.85% and $CaCl_2$ was dissolved in the aqueous phase to a final concentration of 8 g/L prior to emulsification.

Example 9.

A fat spread was prepared as described in Example 5 but the amount of NaCl was reduced to 1.0% and metastable water soluble calcium citrate malate was dissolved in the aqueous phase to a final concentration of 6 g/L.

Example 10.

A fat spread was prepared as described in Example 1 and 3 but 0.06% of a concentrated (α-tocopherol (E307) or lycopene) was added to the oil phase and 0.5% ascorbic acid (E300) was added to the aqueous phase prior to emulsification.

Example 11.

A calcium citrate-whey protein composite was prepared as described in Example 1 but was recovered by filtration and partially dried to obtain a very thick paste. A fat spread was prepared as described in Example 3 but the paste was added to the aqueous phase of the spread alongside other components and was pasteurised prior to emulsification.

Example 12.

Calcium salt-whey protein composites were prepared as described in Examples 1 (calcium citrate) and Example 5 (calcium phosphate) and were recovered by spay-drying. The dried composites were added to the aqueous phase of fat spreads at 7.2 gram (calcium citrate-whey protein composite) and 5 gram (calcium phosphate-whey protein composite) per 100 gram of spread, together with other components and the resulting aqueous phase was used for the preparation of fat spreads as described in Examples 3 or 11 respectively.

Example 13.

A calcium citrate composite was prepared by spray-drying as described in Example 12 and analysed by FT-IR. The spectrum obtained was very similar to that obtained with the calcium citrate composite prepared as described in Example 1 and showed the same characteristic frequency shifts and pattern of bands.

Exampl 14.

A standard yoghurt base was prepared by adding 1.5% by weight of high protein whey powder to pasteurised skimmed milk. 1.5 gram of the calcium citrate-whey composite prepared as described in Example 12 was added per 100 gram of milk and the mixture was homogenised, heated to 80°C and held at this temperature for 30 minutes. The mixture was then cooled to 45°C and the yoghurt mix was inoculated with starter culture containing 1:1 *Lactobacillus bulgaricus* and *Streptococcus thermophilis*.(0.5-0.8% w/v), distributed into containers and incubated at 43°C until pH 4.5 was reached. Typically, the fermentation took about 5 hours. No significant difference between the time required to reach the desired pH was noted between the yoghurts made with and without the calcium containing ingredient. The two yoghurts were virtually indistinguishable organoleptically and on examination with the naked eye.

Example 15.

A yoghurt base was prepared as described in Example 14. The yoghurt base was cooled down to 15°C, and 3% of water and food grade citric acid was added to adjust the pH to about 4.0. 1.9% by weight of citric pectin and 4.1 % by weight of orange essence was added and, after intensive stirring, the mixture was homogenised under pressure and heated to about 50°C and cooled down to 3-5°C to provide a drink.

Example 16.

A milk shake was prepared with calcium-containing composite obtained as described in Example 1 (5%) and non-fat dry milk (6%), whey concentrate (5%), sugar (9%) fructose-dextrose syrup (12%), corn syrup (3%), whey (5%), butter (7.5%), flavouring (0.5%), and water (42%). The syrups and flavouring were added to water combined with the sterol crystals and mixed under high shear with heating up to the pasteurising temperature. Other components were added and, when the sugar dissolved, the mixture was homogenised and cooled directly into a heat-exchanger until the temperature of the product reached about 35°C. The product was stored overnight and then whipped.

Example 17.

A fat spread, a yoghurt and a milk shake were prepared as described in Examples 1, 14 and 16 respectively but Soya isoflavones were added to give an isoflavone content of 100 mg per 100 g of fat spread; 20 mg per serving of yoghurt (125 g) and 30 mg per serving of the milk shake (200 ml). The addition was made at the stage of preparing the aqueous phase (fat spread) breaking the coagulum (yoghurt) and together with syrups and flavouring (milk shake).

CLAIMS

1. A composite material which comprises (1) calcium, (2) insolubilising anion and (3) an additive, where the additive (a) has more than one functional groups selected from the group comprising carboxyl, hydroxyl, amino, amido, thiol and phenol, and any combination thereof and (b) is acceptable for food use.

2. A composite material as described in Claim 1, where the additive is a protein or derived from a protein.

3. A composite material as claimed in Claim 1 or 2, where the additive is a milk derived solid.

4. A composite material as claimed in Claim 3, where the milk derived solid is selected from the group comprising casein, caseinate, whey protein, whey, milk powder, buttermilk and butterfat.

5. A composite material as claimed in any of the Claims 1 to 4, where the insolubilising anion is the conjugate base of an inorganic acid.

6. A composite material as claimed in any of the Claims 1 to 5, where the insolubilising anion is selected from the group comprising phosphate, carbonate, sulphate, pyrophosphate and mixtures thereof.

7. A composite material as claimed in any of the Claims 1 to 4, where the insolubilising anion is the conjugate base of an organic acid.

8. A composite material as claimed in any of the Claims 1 to 4 and 7, where the insolubilising anion is selected from the group comprising citrate,

malate, lactate, citrate malate, propionate, glycerophosphate, gluconate, succinate, ascorbate and mixtures thereof.

9. A method for the preparation of a calcium composite the method comprising combining a source of calcium ions and a source of anions which can produce largely water insoluble calcium in the presence of a third ingredient (additive), which (a) has more than one functional groups selected from the group comprising carboxyl, hydroxyl, amino, amido, thiol and phenol, and any combination thereof and (b) is acceptable for food use.

10. A method as claimed in Claim 9, where the source of calcium ion is selected from the group comprising calcium hydroxide, calcium oxide, calcium carbonate, calcium chloride.

11. A method as claimed in any of the Claims 9 and 10, where the source of anions is selected from the group comprising phosphoric, citric, malic, succinic, carbonic acids and food acceptable salts thereof.

12. A method as claimed in any of the Claims 9 to 11, where the third ingredient is a protein or derived from a protein.

13. A method as claimed in any of the Claims 9 to 11, where the third ingredient is a milk derived solid.

14. A method as claimed in Claim 13, where the milk derived solid is selected from the group comprising casein, caseinate, whey protein, whey, milk powder, buttermilk and butterfat.

15. A method as claimed in any of the Claims 9 to 14, where a calcium source, a source of anions and the third ingredient are combined in aqueous solution at a pH between 2 and 10.

16. A method as claimed in any of the Claims 9 to 15, where the calcium source, the source of anions and the third ingredient are combined at a temperature from 0°C to 95°C, with stirring.

17. A method as claimed in any of the Claims 8 to 16, where the calcium composite is dried.

18. A calcium salt composite obtainable by the method of any one of Claims 9 to 17.

19. A method of supplementing a food product or beverage with calcium the method comprising the step of including in the food product or beverage a calcium composite according to any one of Claims 1 to 8 or 18.

20. A method according to Claim 19 wherein the calcium composite is formed *in situ* during the preparation of the food product or beverage.

21. A food product or beverage supplemented with calcium obtainable by the method of Claims 19 or 20.

22. A food product or beverage containing a calcium composite according to any one of Claims 1 to 8 or 18.

23. The use of the composite as claimed in any of the Claims 1 to 8 or 18 in food products, drinks and food supplements.

24. The use of the composite prepared by the method as claimed in any of the Claims 9 to 16 in food products, drinks and supplements.

25. The use of the composite as claimed in any of the Claims 23 and 24, where the food products are fat spreads.

26. The use of the composite as claimed in any of the Claims 23 and 24, where the food products are yoghurts.

27. The use of the composite as claimed in any of the Claims 23 and 24, where the drinks are yoghurt drinks.

28. A food product or beverage according to Claim 21 or 22 or obtained by the method of Claims 19 or 20 which is additionally supplemented with another physiologically active food additive which can be shown to be beneficial to human health.

29. A food product or beverage according to Claim 28 wherein the additional food additive is selected from the group consisting of vitamins, minerals, plant sterols, lycopenes, carotenoids, flavonoids, isoflavones, antioxidants, lutein and mixtures thereof.

30. A food product or beverage according to Claim 29 wherein the food additive is soya isoflavone added in excess of 10 mg per serving of the food product or beverage.

31. A food product according to Claim 21 or 22 or obtained by the methods of Claim 19 or 20 which is an emulsified fat spread.

32. An emulsified fat spread which is supplemented with calcium, where the calcium source is included in the aqueous phase of the product composition in a largely insoluble form obtainable by the method of Claim 19 or 20.

33. An emulsified fat spread which is supplemented with calcium, where the calcium source is included in the aqueous phase of the product composition in a largely insoluble form.

34. An emulsified fat spread which is supplemented with calcium, where the calcium source is included in the aqueous phase of the product

composition in a largely insoluble form and where the aqueous phase of the product composition contains milk derived solids.

35. An emulsified fat spread as claimed in any one of Claims 32 to 34, where the calcium source comprises calcium and an insolubilising anion of an organic acid, and is present in a largely insoluble form.

36. An emulsified fat spread as claimed in any one of Claims 32 to 34, where the calcium source comprises calcium and an insolubilising anion of an inorganic acid, and is present in a largely insoluble form.

37. An emulsified fat spread as claimed in any of the Claims 32 to 36, where the spread contains an additional water soluble calcium salt.

38. An emulsified fat spread as claimed in Claim 37, where the largely water insoluble calcium source contains an insolubilising anion of an organic acid and the water soluble calcium salt is a salt of an organic acid.

39. An emulsified fat spread as claimed in Claim 37, where the largely water insoluble calcium source contains insolubilising anion of an inorganic acid and the water soluble calcium salt is a salt of an organic acid.

40. An emulsified fat spread as claimed in Claim 37, where the largely water insoluble calcium source contains an insolubilising anion of an organic acid and the water soluble calcium salt is a calcium salt of an inorganic acid.

41. An emulsified fat spread as claimed in Claim 37, where the largely water insoluble calcium source contains insolubilising anion of an inorganic acid and the water soluble calcium salt is a calcium salt of an inorganic acid.

42. An emulsified fat spread as claimed in any of the Claims 32 to 41, where the insolubilising anion is selected from the group comprising citrate,

malate, lactate, citrate malate, propionate, glycerophosphate, gluconate, succinate, ascorbate and mixtures thereof.

43. An emulsified fat spread as claimed in any of the Claims 32 to 41, where the insolubilising anion of an inorganic acid is selected from the group comprising carbonate, phosphate, pyrophosphate, sulphate, chloride, and mixtures thereof.

44. An emulsified fat spread as claimed in any of the Claims 32 to 43, where milk derived solids are selected from the group consisting of casein, caseinate, whey protein, whey, milk powder, buttermilk and butterfat.

45. An emulsified fat spread as claimed in any of the Claims 32 to 44, which is further supplemented with another physiologically active food additive which can be shown to be beneficial to human health in addition to those required by legislation.

46. An emulsified fat spread as claimed in Claim 45 where the further physiologically active food additive is selected from the group consisting of vitamins, minerals, plant sterols, lycopenes, carotenoids, flavonoids, isoflavones, antioxidants, lutein and mixtures thereof.

47. An emulsified fat spread as claimed in Claim 45 where the further food additive is soya isoflavone added in excess of 10 mg per serving.

48. An emulsified fat spread as claimed in any of the Claims 32 to 47, which contains less than 40% fat.

49. A process for the production of emulsified fat spreads as claimed in any of the Claims 32 to 48, which comprises of contacting (i) milk derived solids and (ii) a source of calcium ions and (iii) a source of insolubilising

anions which can produce a largely water insoluble calcium salt, in the aqueous phase of the product composition prior to emulsification.

50. A process for the production of emulsified fat spreads as claimed in any of the Claims 32 to 48, where the combined milk derived solids, the calcium source and the source of insolubilising anions which can produce a largely water insoluble calcium salt, are treated at a temperature and exposure time combination which is sufficient for pasteurisation.

51. An emulsified fat spread as claimed in any one of Claim 32 to 48 which contains the composite material as claimed in any one of Claims 1 to 8 and 18.

52. An emulsified fat spread as claimed in any one of Claims 32 to 48 which contains the composite material as claimed in any one of Claims 9 to 17.

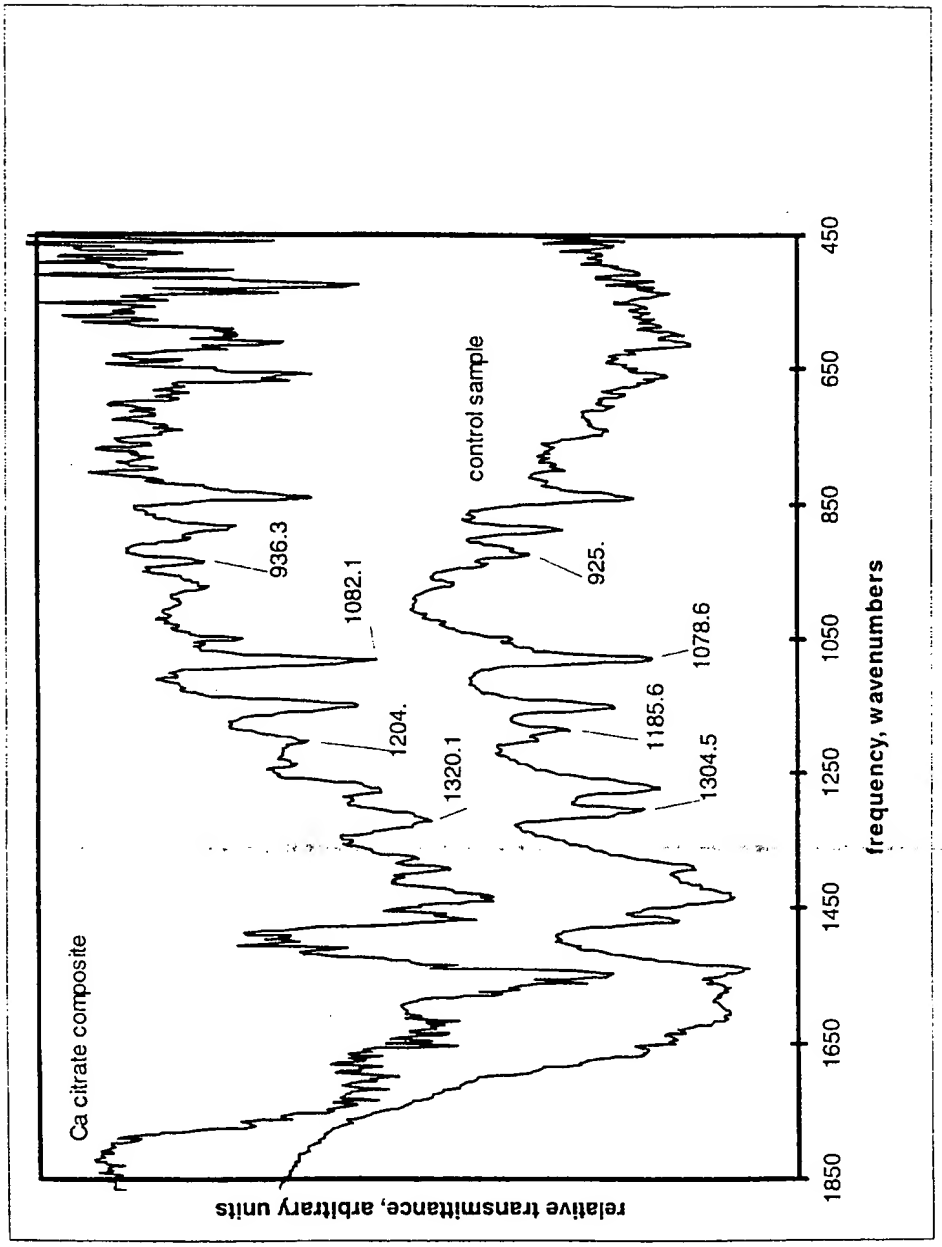
53. A food supplement containing the composite material as claimed in any one of Claims 1 to 8 and 18.

54. A food supplement according to Claim 53 which is a tablet containing the composite material and a binding agent.

55. A food supplement according to Claim 53 which is a capsule containing the composite material.

56. A food supplement according to Claim 53 which is a suspension of the composite material in a food acceptable liquid.

Figure 1


Ca citrate composite
control sample
936.3
1082.1
1204.
1320.1
925.
1078.6
1185.6
1304.5
relative transmittance, arbitrary units
frequency, wavenumbers
1850
1650
1450
1250
1050
850
650
450

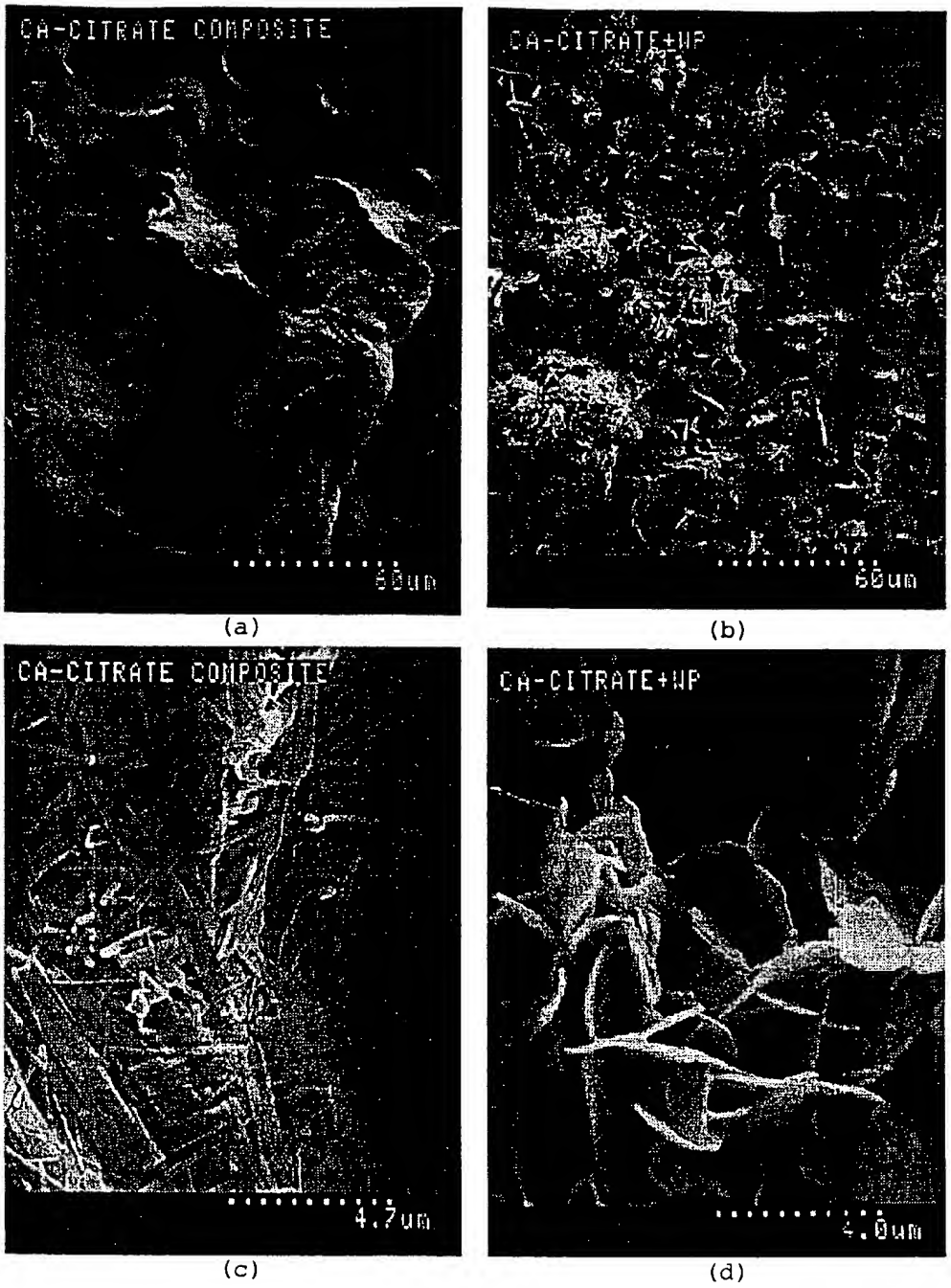

CA-CITRATE COMPOSITE
60um
(a)
CA-CITRATE+HP
60um
(b)
CA-CITRATE COMPOSITE
4.7um
(c)
CA-CITRATE+HP
4.0um
(d)

Figure 2

2/4

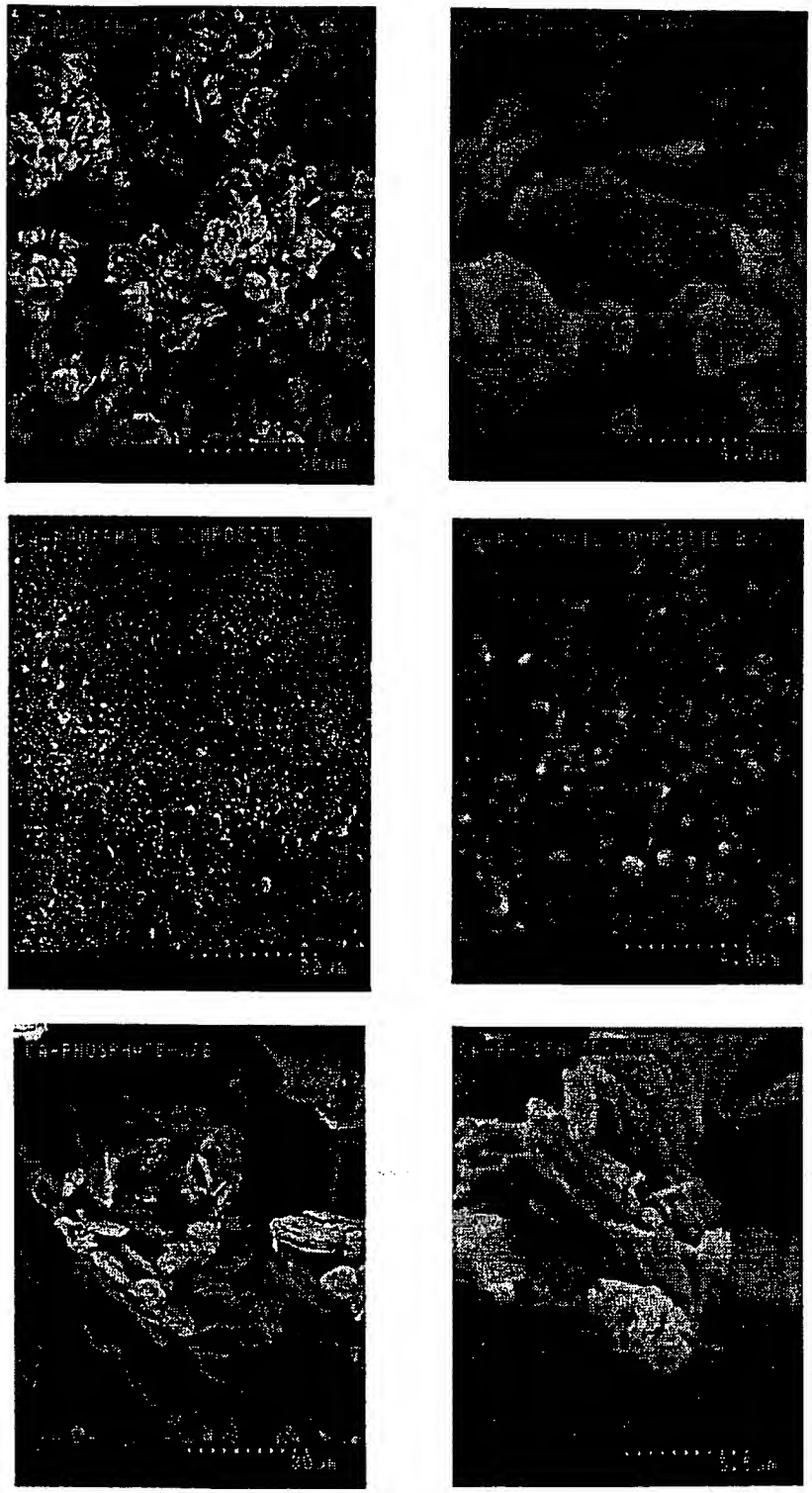


Figure 3

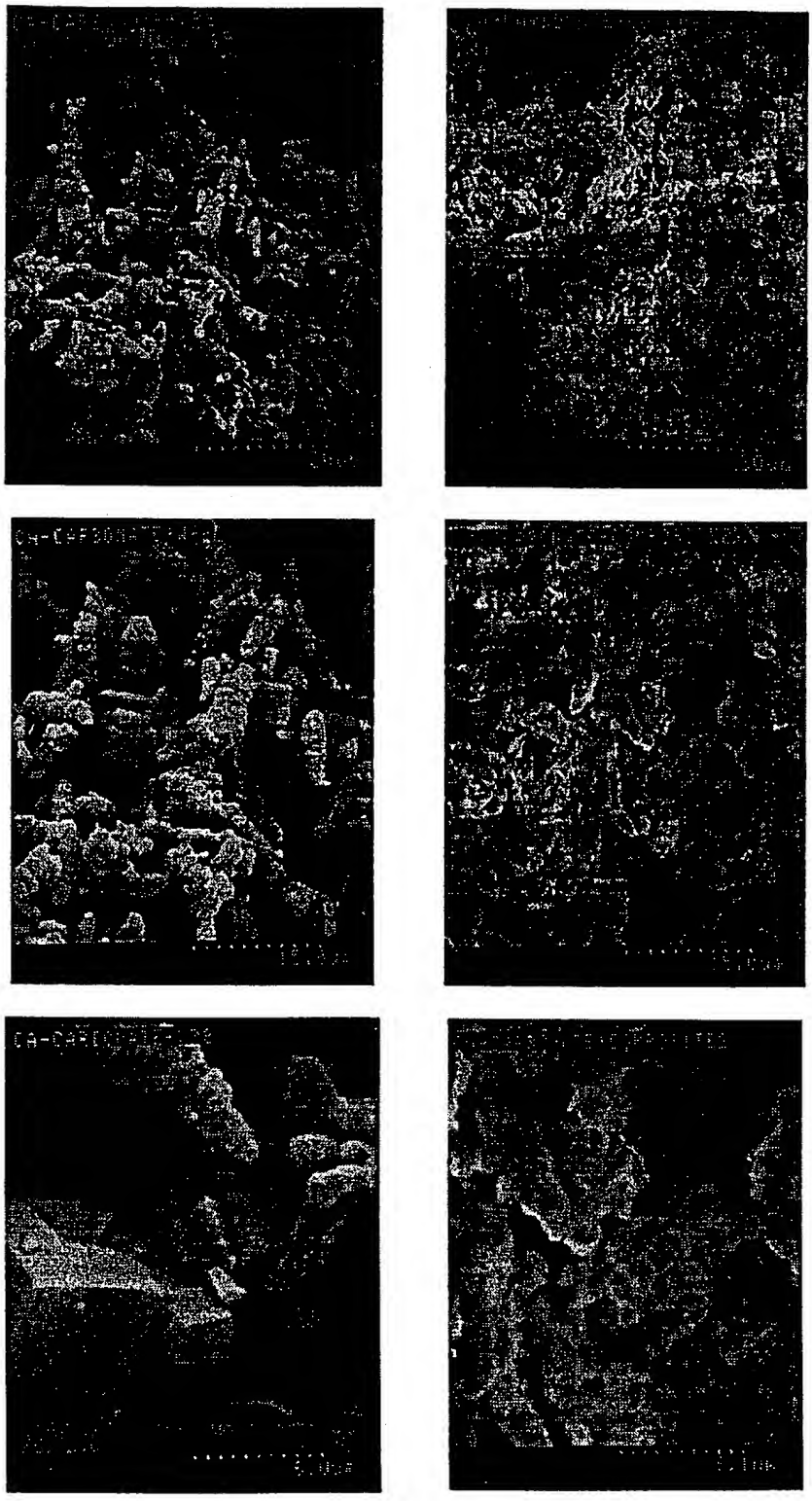


Figure 4

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB 00/00355

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A23L1/304 A23D7/00 A23D7/015 A23D7/02 A23L2/52
A23L2/66 A23C9/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A23L A23D A23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 614 612 A (GEN FOODS INC) 14 September 1994 (1994-09-14) page 2, line 50 -page 5, line 45; examples ---	1-25, 28-31, 53-56
X	US 5 766 330 A (KJELSBERG LYNNE M ET AL) 16 June 1998 (1998-06-16) abstract; examples column 5, line 46 -column 7, line 33 ---	1-24, 26-31, 53-56
X	EP 0 550 123 A (GEN FOODS INC) 7 July 1993 (1993-07-07) page 2, line 21 -page 4, line 36; examples --- -/--	1-24, 53-56

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 May 2000	24/05/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Boddaert, P

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB 00/00355

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 48637 A (DAVISCO FOODS INT INC) 5 November 1998 (1998-11-05) page 4, line 26 -page 10, line 7; claims; examples	1-24, 53-56
P,X	WO 99 18806 A (DAVISCO FOODS INT INC) 22 April 1999 (1999-04-22) page 4, line 7 -page 11, line 2	1-24,26, 27,53-56
A	EP 0 549 290 A (GEN FOODS INC) 30 June 1993 (1993-06-30) cited in the application the whole document	1-56
X	WO 98 48638 A (DAVISCO FOODS INT INC) 5 November 1998 (1998-11-05) page 6, line 14 -page 15, line 8; claims; examples	1-56
A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 05, 31 May 1996 (1996-05-31) & JP 08 000220 A (OTSUKA SHOKUHIN KK), 9 January 1996 (1996-01-09) abstract	
A	GB 892 914 A (OHTAKI) 4 April 1962 (1962-04-04) page 1, line 8 -page 2, line 5; examples	1-53

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ional Application No
PCT/GB 00/00355

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0614612 A	14-09-1994	US 5258190 A	02-11-1993
		CA 2114997 A	11-09-1994
		CZ 9400300 A	15-12-1994
		HU 69632 A	28-09-1995
		PL 174303 B	31-07-1998
		SK 24394 A	05-01-1995
US 5766330 A	16-06-1998	AU 5618398 A	17-07-1998
		EP 0948569 A	13-10-1999
		PL 334249 A	14-02-2000
		WO 9828367 A	02-07-1998
EP 0550123 A	07-07-1993	US 5219602 A	15-06-1993
		AU 651199 B	14-07-1994
		AU 1610592 A	24-06-1993
		BR 9201994 A	22-06-1993
		CA 2067943 A	21-06-1993
		CN 1073333 A	23-06-1993
		FI 922166 A	21-06-1993
		JP 5260906 A	12-10-1993
		MX 9202413 A	01-06-1993
		NO 922031 A	21-06-1993
		NZ 242853 A	27-06-1994
WO 9848637 A	05-11-1998	AU 7266198 A	24-11-1998
WO 9918806 A	22-04-1999	AU 9501098 A	03-05-1999
EP 0549290 A	30-06-1993	US 5194270 A	16-03-1993
		AT 134109 T	15-02-1996
		CA 2084468 A	21-06-1993
		DE 69208346 D	28-03-1996
		DE 69208346 T	19-09-1996
		DK 549290 T	11-03-1996
		ES 2084297 T	01-05-1996
		FI 925789 A	21-06-1993
		NO 924832 A	21-06-1993
		US 5258190 A	02-11-1993
WO 9848638 A	05-11-1998	AU 7247498 A	24-11-1998
JP 08000220 A	09-01-1996	NONE	
GB 892914 A		NONE	